

The 4f-ligand hybridization in the evolution of heavy-fermion behaviour in the series  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 8983

(<http://iopscience.iop.org/0953-8984/12/42/305>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:54

Please note that [terms and conditions apply](#).

## The 4f-ligand hybridization in the evolution of heavy-fermion behaviour in the series $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$

C Tien<sup>†</sup>, L Y Jang<sup>‡</sup>, C Y Kuo<sup>†</sup>, J J Lu<sup>†</sup> and S W Feng<sup>†</sup>

<sup>†</sup> Department of Physics, National Cheng Kung University, Tainan, Taiwan, Republic of China

<sup>‡</sup> Synchrotron Radiation Research Centre, Hsinchu, Taiwan, Republic of China

Received 5 July 2000, in final form 21 August 2000

**Abstract.**  $\text{CeRu}_2\text{Si}_2$  is a heavy-fermion compound and  $\text{CeNi}_2\text{Si}_2$  is a mixed-valence compound. We measured the  $L_{\text{III}}$  absorption spectra of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  ( $x = 0, 0.2, 0.4, 0.8, 0.9, 1.0, 1.1, 1.4, 1.6,$  and  $2.0$ ) at 16, 50, 100, 200, and 300 K. The linear coefficient of the specific heat  $\gamma$  of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  is enhanced rapidly for Ce valence  $v < 3.08$ . The structure of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  is consistent with the tetragonal space group  $I4/mmm$ . There is no critical lattice constant  $c$  separating the strongly mixed-valence regime from the heavy-fermion regime for  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$ . The value of the lattice constant  $c$  is almost a linear function of  $x$ , whereas there is a deviation from linearity for the values of the lattice constant  $a$  when  $x < 0.4$ . Judging by the  $L_{\text{III}}$  x-ray absorption spectra of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  and  $\text{CeRu}_2\text{Si}_{2-x}\text{Ge}_x$ , the evolution from heavy-fermion to mixed-valence behaviour might be due just to the hybridization between the Ce 4f-electron wave function and the sp wave function of Ru.

### 1. Introduction

The heavy-fermion (HF) [1] and mixed-valence (MV) [2] phenomena in rare-earth and actinide compounds have been studied for more than thirty years. Although the factors that lead to the formation of a heavy-fermion state are still not completely known, it is believed that the hybridization of the highly correlated f electron with the itinerant conduction electrons should be responsible for both HF and MV behaviours. It was pointed out by Meisner *et al* [3] that, even beyond Hill's limit for the separation of f atoms where the f–f overlap is negligible, there is a correlation between f–f atomic separation and the values of the linear coefficient of the specific heat ( $\gamma$ ). However, Koelling, Dunlap, and Crabtree [4] attributed the anomalous HF properties to the f-ligand hybridization. A systematic study of alloying at the ligand site is one of the best methods for achieving an understanding of the influence of the ligands on the origin of the heavy fermions.

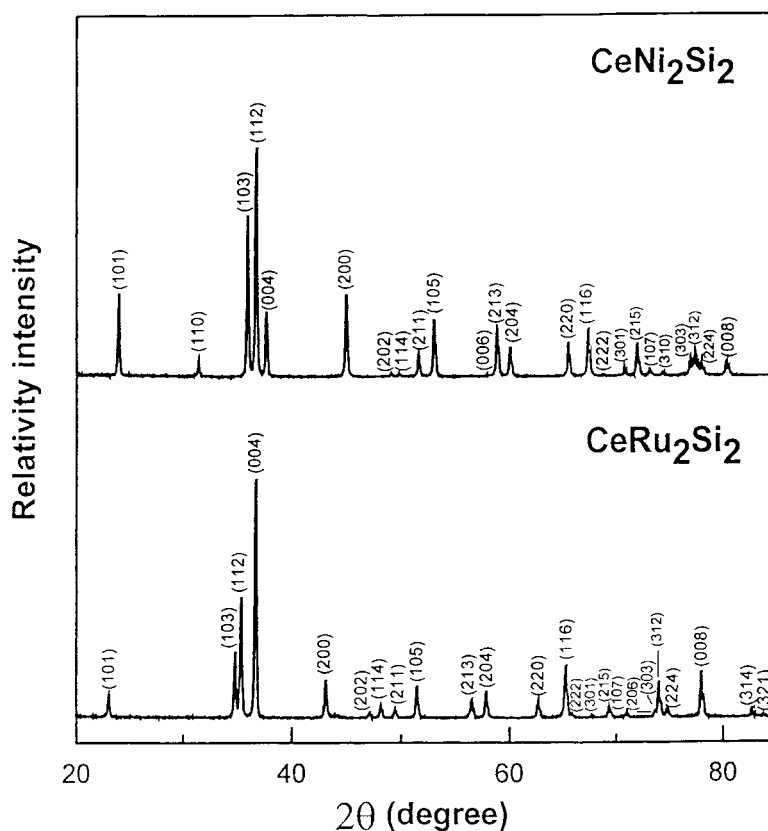
Among the compounds of the  $\text{ThCr}_2\text{Si}_2$  type,  $\text{CeCu}_2\text{Si}_2$  is a well-known HF system and  $\text{CeNi}_2\text{Si}_2$  is a strongly mixed-valence compound. The evolution of heavy-fermion behaviour in the  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  system was studied by Sampathkumaran and Vijayaraghavan [5]. For  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$ , heavy-fermion behaviours are destroyed for  $x \sim 0.65$ . There is an anomalous increase in the Ce–ligand distance without any anomaly in the Ce–Ce separation for  $x < 0.65$ . Comparing the properties of  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  with another pseudoternary series of the  $\text{ThCr}_2\text{Si}_2$  type could further clarify the relation between the 4f-ligand hybridization and heavy fermions.

In this paper, we report results for  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$ .  $\text{CeRu}_2\text{Si}_2$  is a widely studied compound [6, 7] and its  $\gamma$ -value is about  $400 \text{ mJ mol}^{-1} \text{ K}^{-2}$ .  $\text{CeRu}_2\text{Si}_2$  is one of the few cases of heavy-fermion compounds for which no evidence of long-range magnetic ordering has

been found down to  $\sim 20$  mK. To the best of our knowledge, the influence of 4f-ligand dehybridization on the evolution of heavy-fermion behaviour in  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  has still not been investigated.

## 2. Experimental methods

Polycrystalline samples of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  were prepared by arc melting the pure elements in their stoichiometric ratio in an atmosphere of purified argon gas. The button was flipped several times and remelted to achieve good homogeneity. The samples were annealed at 1100 K for eight days. The overall weight loss during melting was less than 1%. X-ray measurements of the sample were carried out at room temperature and showed only a single phase in these series of samples. The structure is consistent with the tetragonal space group  $I4/mmm$ . Figure 1 shows the x-ray diffraction patterns of  $\text{CeRu}_2\text{Si}_2$  and  $\text{CeNi}_2\text{Si}_2$ . The lattice parameters of  $\text{CeRu}_2\text{Si}_2$  are  $a = 4.192 \text{ \AA}$ ,  $c = 9.794 \text{ \AA}$ , which are consistent with the report of Godart *et al* [8]. The lattice parameters of  $\text{CeNi}_2\text{Si}_2$  are  $a = 4.032 \text{ \AA}$ ,  $c = 9.558 \text{ \AA}$ , which are consistent with the report of Ammarguella *et al* [9].



**Figure 1.** The x-ray diffraction patterns of  $\text{CeRu}_2\text{Si}_2$  and  $\text{CeNi}_2\text{Si}_2$ .

The  $L_{\text{III}}$  x-ray absorption spectroscopy (XAS) spectra of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  were measured at the SRRC (Synchrotron Radiation Research Centre, Hsinchu, Taiwan, ROC) on the wiggler x-ray beamline BL17C (Ce  $L_{\text{III}}$ -edge measurements). The samples used for the XAS

measurements were prepared by dusting the well-powdered samples onto Scotch tape. It was ensured that the size of the powder particles was smaller than  $37 \mu\text{m}$  by using a 400-mesh sieve to avoid the thickness effect [10].

Specific-heat measurements of  $C(T)$  were performed in a Quantum Design PPMS (Physical Property Measurement System).  $C/T$  for  $CeNi_2Si_2$  is  $\sim 33 \text{ mJ mol}^{-1} \text{ K}^{-2}$  which agrees with the report of Kuentzler *et al* [11]. The magnetic specific heat is defined as

$$C_m(T) = C(CeRu_{2-x}Ni_xSi_2) - C(LaRu_{2-x}Ni_xSi_2).$$

$\gamma_m$  for  $CeRu_2Si_2$  is  $\sim 350 \text{ mJ mol}^{-1} \text{ K}^{-2}$  which agrees very well with those found in the report of van der Meulen *et al* [12].

### 3. Experimental results

#### 3.1. $L_{III}$ x-ray absorption spectroscopy results

$L_{III}$  x-ray absorption spectroscopy (XAS) is a very useful tool for measuring the valence in mixed-valence systems [13–15]. Figure 2 shows the Ce  $L_{III}$ -edge spectra of  $CeRu_{2-x}Ni_xSi_2$  for  $x = 2.0, 1.6, 1.4, 1.1, 1.0, 0.9, 0.8, 0.4, 0.2,$  and  $0.0$  at  $300 \text{ K}$ . To compare the intensity in the Ce peak region, all spectra are normalized to the  $Ce^{3+}$  peak. As shown in table 1, by fitting the  $L_{III}$  spectra with a superposition of  $Ce^{3+}$  and  $Ce^{4+}$  edges, one obtains the Ce valences of  $CeRu_{2-x}Ni_xSi_2$ . The details of the fitting procedure have been discussed elsewhere [13, 16]. As shown in table 1, the valence of Ce in  $CeNi_2Si_2$  at  $300 \text{ K}$  is  $v = 3.18$  which agrees very well with those found in the reports of Edwards *et al* [17] and Liang [13]. Also, in our measurements, the Ce valence of  $CeRu_2Si_2$  at  $300 \text{ K}$  is  $v = 3.03$  which is also consistent with the measurement of Tsunekawa *et al* [18].

**Table 1.** The valence of Ce in  $CeRu_{2-x}Ni_xSi_2$  at 300, 200, 100, 50, and 16 K.

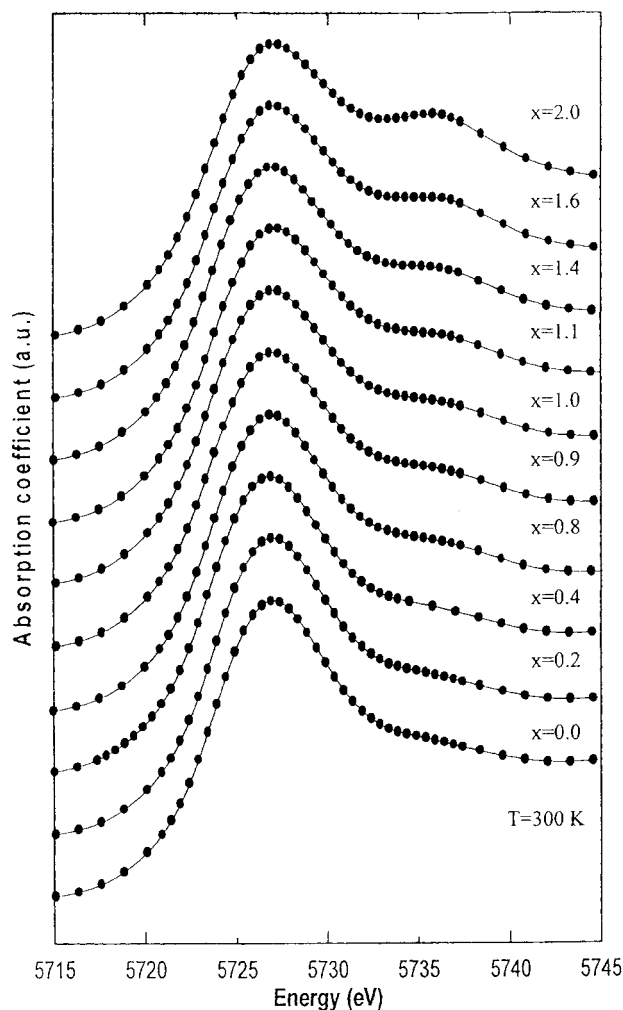
$x$	16 K	50 K	100 K	200 K	300 K
2	3.198	3.198	3.191	3.186	3.178
1.6	3.190	3.189	3.145	3.169	3.145
1.4	3.178	3.176	3.170	3.155	3.136
1.1	3.163	3.161	3.153	3.139	3.123
1	3.154	3.149	3.144	3.127	3.113
0.9	3.139	3.135	3.127	3.108	3.096
0.8	3.108	3.107	3.097	3.082	3.070
0.4	3.078	3.074	3.067	3.060	3.055
0.2	3.051	3.049	3.046	3.044	3.040
0	3.029	3.028	3.028	3.029	3.030

#### 3.2. Lattice parameter results

The lattice parameters  $a$  and  $c$  of  $CeRu_{2-x}Ni_xSi_2$  are shown in table 2. For  $CeRu_{2-x}Ni_xSi_2$  the value of  $c$  is almost a linear function of  $x$  within the limits of the experimental error, whereas the value of  $a$  shows a strong deviation from the linear behaviour for  $x < 0.8$ .

#### 3.3. Specific-heat results

Figure 3 shows the specific heat versus temperature,  $C(T)/T$  versus  $T^2$ , for  $CeRu_2Si_2$  and  $LaRu_2Si_2$  between 5 and 20 K. The inset of figure 3 shows  $C/T$  versus  $T^2$  for  $CeRu_2Si_2$



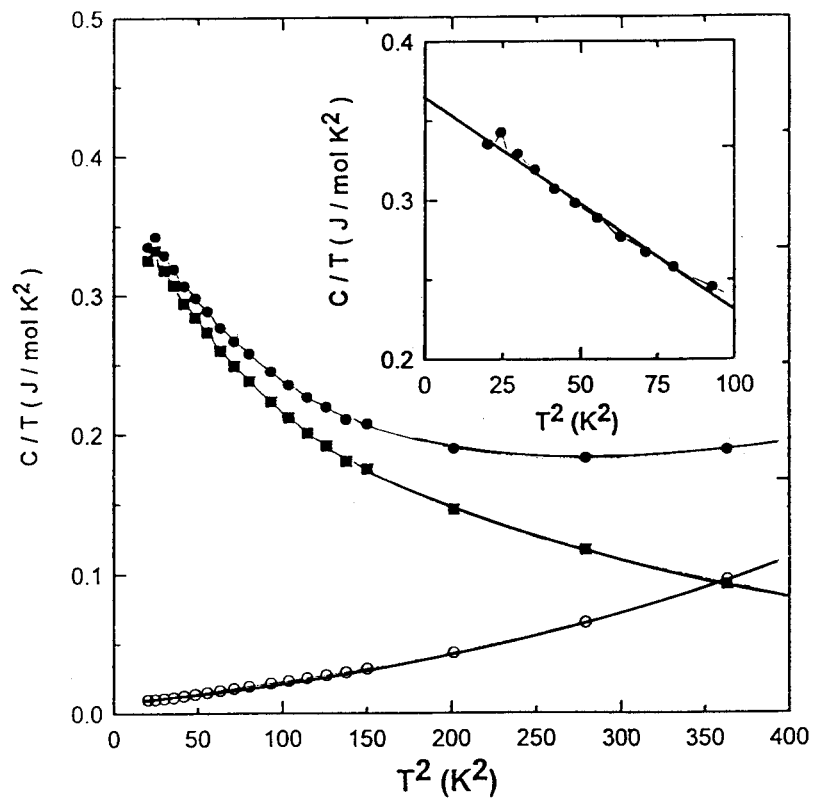
**Figure 2.** The Ce L<sub>III</sub>-edge spectra of CeRu<sub>2-x</sub>Ni<sub>x</sub>Si<sub>2</sub>. To compare the intensity in the Ce peak region, all spectra are normalized to the Ce<sup>3+</sup> peak.

below 10 K. The solid line through the data represents a fit to  $C(T) = \gamma T + \beta T^3$  with  $\gamma = 355 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\beta = -1.21 \text{ mJ mol}^{-1} \text{ K}^{-4}$ . Below 10 K, the magnetic specific heat  $C_m(T)$  of CeRu<sub>2-x</sub>Ni<sub>x</sub>Si<sub>2</sub> can be fitted by  $C_m(T) = \gamma_m T + \beta_m T^3$ .  $\gamma_m$  for CeRu<sub>2</sub>Si<sub>2</sub> is  $\sim 350 \text{ mJ mol}^{-1} \text{ K}^{-2}$  which agrees very well with those found in the report of van der Meulen *et al* [12].

Figure 4 shows the specific heat versus temperature,  $C(T)/T$  versus  $T^2$ , for CeNi<sub>2</sub>Si<sub>2</sub> and LaNi<sub>2</sub>Si<sub>2</sub> between 2 and 40 K. The inset of figure 4 shows  $C/T$  versus  $T^2$  for CeNi<sub>2</sub>Si<sub>2</sub> below 14 K. The solid line through the data represents a fit to  $C(T) = \gamma T + \beta T^3$  with  $\gamma = 32.6 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\beta = 0.22 \text{ mJ mol}^{-1} \text{ K}^{-4}$ . The  $\gamma$ -value of CeNi<sub>2</sub>Si<sub>2</sub> is quite typical for a MV material such as CeMn<sub>2</sub>Si<sub>2</sub> [19]. Above 30 K, the specific heat of CeNi<sub>2</sub>Si<sub>2</sub> equals that of LaNi<sub>2</sub>Si<sub>2</sub>. As shown in the inset of figure 4, there is a small peak around 6 K. Below 10 K,  $\gamma_m = C_m/T$  for CeNi<sub>2</sub>Si<sub>2</sub> is  $\sim 30 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . For both CeRu<sub>2</sub>Si<sub>2</sub> and

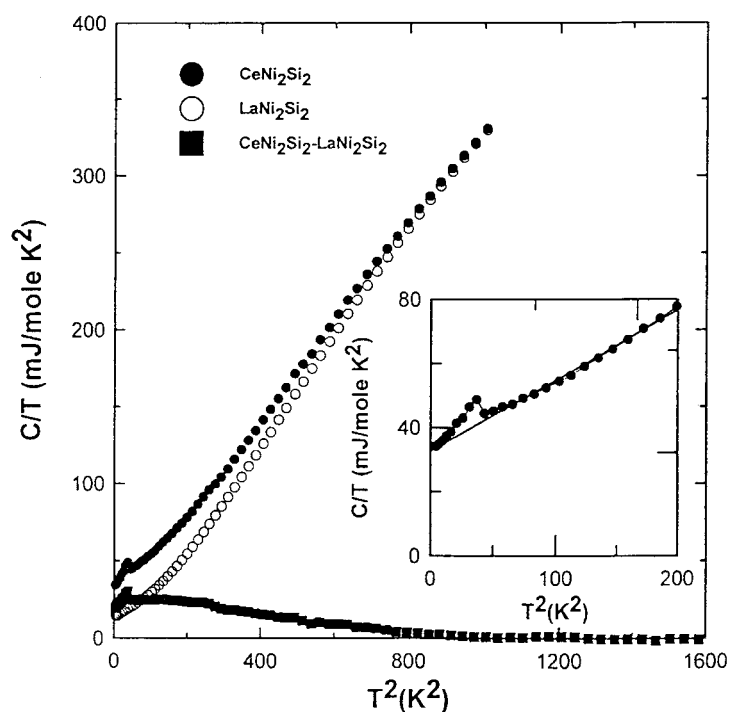
**Table 2.** Lattice constants and unit-cell volumes of  $CeRu_{2-x}Ni_xSi_2$ .

$x$	$a$ (Å)	$c$ (Å)	$c/a$	Cell volume (Å <sup>3</sup> )	Valence (at 300 K)
2	4.032	9.558	2.370	155.423	3.178
1.6	4.051	9.595	2.373	157.490	3.145
1.4	4.053	9.621	2.370	158.068	3.136
1.1	4.070	9.645	2.370	159.750	3.123
1	4.086	9.649	2.361	161.076	3.113
0.9	4.091	9.680	2.366	162.014	3.096
0.8	4.098	9.704	2.368	162.939	3.070
0.4	4.163	9.771	2.347	169.327	3.055
0.2	4.188	9.783	2.336	171.615	3.040
0	4.192	9.793	2.336	172.128	3.030

**Figure 3.**  $C/T$  (●) and  $C_m/T$  (■) for  $CeRu_2Si_2$  versus  $T^2$ . The open circles (○) show  $C/T$  for  $LaRu_2Si_2$  versus  $T^2$ . The inset shows  $C/T$  versus  $T^2$  below 10 K.

$CeNi_2Si_2$ ,  $\gamma \sim \gamma_m$ . The same kind of behaviour was observed for other compounds of the  $CeCu_{2-x}Ni_xSi_2$  system.

Figures 5 and 6 show  $C(T)/T$  versus  $T^2$  for  $CeCu_{2-x}Ni_xSi_2$  between 2 and 14 K for  $x = 1.8, 1.6, 1.4, 1.0, 0.8, 0.6, 0.4$ , and 0.2. The solid line through the data represents a fit to  $C(T) = \gamma T + \beta T^3$  between 7 and 14 K. The coefficients  $\gamma$  and  $\beta$  for  $CeRu_{2-x}Ni_xSi_2$  are



**Figure 4.**  $C/T$  (●) for  $\text{CeNi}_2\text{Si}_2$  and  $C/T$  (■) for  $\text{LaNi}_2\text{Si}_2$  versus  $T^2$ . The open circles (○) show  $C/T$  for  $\text{LaNi}_2\text{Si}_2$  versus  $T^2$ . The inset shows  $C/T$  for  $\text{CeNi}_2\text{Si}_2$  versus  $T^2$  below 14 K.

shown in table 3. As shown in figures 5 and 6, no matter how carefully we prepare samples, the small peak around 6 K always exists.

Kuentzler *et al* [11] reported that for  $x > 0.3$ , the plot of  $C/T$  versus  $T^2$  for  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  exhibits a very weak peak around 6 K. Kuentzler *et al* claimed that this anomaly is due to magnetic oxide impurities. Liang *et al* [19] and Mihalisin *et al* [20] also observed very similar 6 K peaks for  $\text{CeMn}_2\text{Si}_2$  and  $\text{CePd}_3$ .

The linear coefficient of the specific heat  $\gamma$  and the valence  $v$  of Ce for  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  are shown in table 3. When  $v < 3.08$ ,  $\gamma$  increases rapidly, which also indicates  $v \sim 3.08$  as

**Table 3.** The  $\gamma$ - and  $\beta$ -values of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$ .

$x$	$\gamma$ ( $\text{mJ mol}^{-1} \text{K}^{-2}$ )	$\beta$ ( $\text{mJ mol}^{-1} \text{K}^{-4}$ )	Valence (at 300 K)
2	32.66	0.22	3.178
1.8	33.05	0.19	3.159
1.6	38.09	0.17	3.145
1.4	40.93	0.23	3.136
1.0	52.28	0.16	3.113
0.8	64.88	0.20	3.070
0.6	83.52	0.22	3.059
0.4	129.13	0.24	3.055
0.2	189.73	0.08	3.040
0	355.05	-1.21	3.030

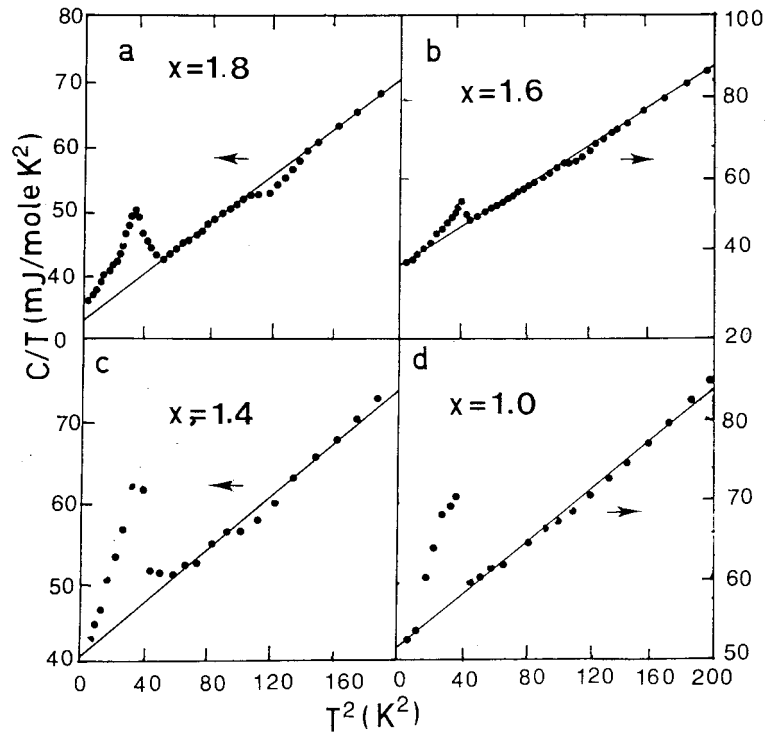


Figure 5.  $C/T$  for  $CeRu_{2-x}Ni_xSi_2$  versus  $T^2$  for  $x = 1.8, 1.6, 1.4,$  and  $1.0$ .

the valence at the crossover from MV to HF behaviour. The relation between  $\gamma$  and the Ce valence  $v$  can be described by  $\gamma = \gamma_0(1 - n_f)^{-1}$ , where  $n_f = 4 - v$  is the Ce 4f occupation number [21].

#### 4. Discussion

The evolution of heavy-fermion behaviour in the  $CeCu_{2-x}Ni_xSi_2$  system was reported by Sampathkumaran and Vijayaraghavan [5]. In  $CeCu_{2-x}Ni_xSi_2$ , the Ce–Ce distance is much larger than the Hill limit [22]. Therefore, the direct overlap of 4f wave functions located on different Ce atoms is not responsible for the HF and MV behaviours. The localization of 4f electrons essentially occurs through hybridization of the f-electron wave function with the sp or s wave function of the neighbouring (Cu or Si) atoms. For  $CeCu_{2-x}Ni_xSi_2$ , the value of the lattice parameter  $a$  is an almost linear function of  $x$  and the value of the lattice parameter  $c$  deviates from linearity for  $x < 0.65$ . Usually in cerium compounds of the  $ThCr_2Si_2$  type, any anomaly in the valence of Ce is expected to influence the lattice constant  $a$  predominantly and the values of  $c$  will reflect anomalous Ce–ligand bonding effects [5, 23]. Since the value of  $a$  is a smooth function of  $x$  for  $CeCu_{2-x}Ni_xSi_2$ , Sampathkumaran and Vijayaraghavan [5] suggested that the dependence of the Ce valence on  $x$  in this system is linear. Since for  $c > 9.8 \text{ \AA}$  ( $x \sim 0.5$ ), the value of  $c$  deviates from linearity and the zero-temperature susceptibility of  $CeCu_{2-x}Ni_xSi_2$  is enhanced significantly, Sampathkumaran and Vijayaraghavan suggested that the dehybridization of the ligand-valence band from the Ce 4f band is essential to attain the heavy-fermion ground state. Also, they claimed that there might be a critical Ce ligand (or  $c$ ),



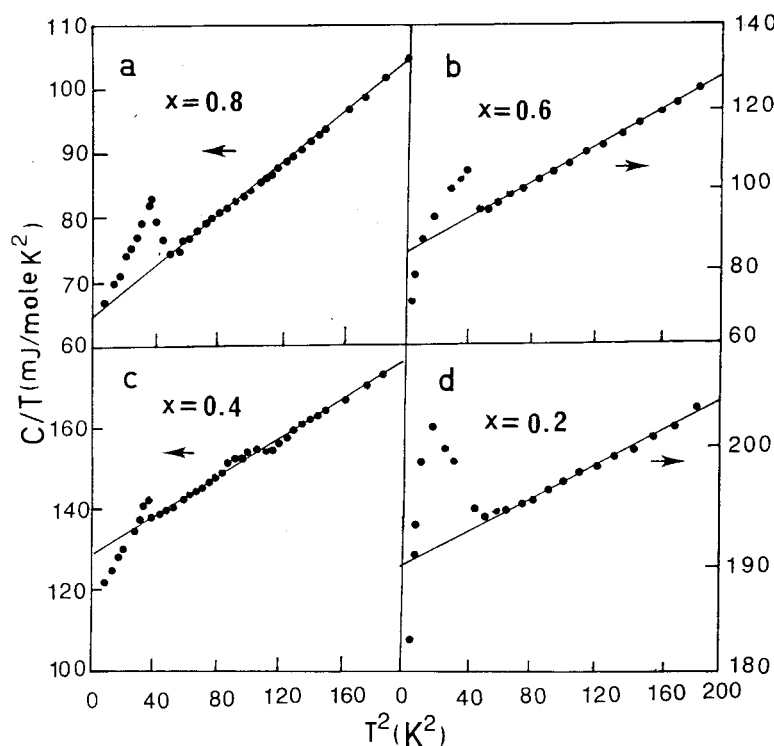


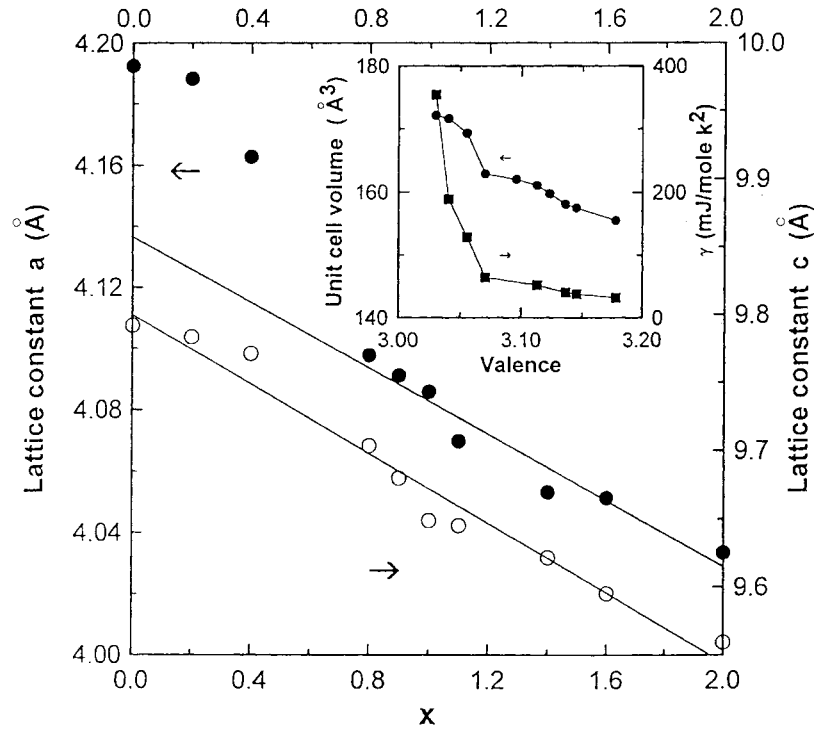
Figure 6.  $C/T$  for  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  versus  $T^2$  for  $x = 0.8, 0.6, 0.4,$  and  $0.2$ .

$c \sim 9.8 \text{ \AA}$ , separating the strongly mixed-valence regime from the heavy-fermion regime in cerium compounds with  $\text{ThCr}_2\text{Si}_2$  structure.

Ce  $L_{\text{III}}$  x-ray absorption spectroscopy for  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  was reported by Liang [13]. The Ce valence for  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  is a smooth function of  $x$ . Comparing Ce valences  $v$  with the values of the specific-heat coefficient  $\gamma$  from the report of Kuentzler *et al* [11], the  $\gamma$ -values are enhanced rapidly for  $v < 3.08$  (with  $x < 0.4$ ). Therefore, 3.08 is the valence in the crossover region where  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  crosses from a heavy-fermion to a mixed-valence state.

The lattice parameters  $a$  and  $c$  of  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  are plotted versus  $x$  in figure 7. In contrast with the case for  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$ , as shown in figure 7, for  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$ , the value of  $c$  is almost a linear function of  $x$ , whereas there is a deviation from linearity for the values of  $a$  when  $x < 0.4$ . There is no critical lattice constant  $c$  that separates the strongly mixed-valence regime from the heavy-fermion regime for  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$ . The inset of figure 7 shows the valence  $v$  of Ce versus the unit-cell volume, and when  $v < 3.08$  the lattice constant  $a$  increases rapidly, which suggests that  $v \sim 3.08$  is the valence at the crossover from MV to HF behaviour. As indicated in the inset of figure 3, the  $\gamma$ -value is enhanced rapidly for  $v < 3.08$ . We obtain the same result that  $\text{CeCu}_{2-x}\text{Ni}_x\text{Si}_2$  and  $\text{CeRu}_{2-x}\text{Ni}_x\text{Si}_2$  cross from heavy-fermion to mixed-valence states at  $v \sim 3.08$ .

On the basis of inelastic neutron scattering, Loidl *et al* [24] claimed that for ternary compounds of  $\text{ThCr}_2\text{Si}_2$ -type structure with large unit-cell volume, the RKKY interaction among well-localized f electrons dominates, and the compounds will form an RKKY anti-ferromagnetic state. With a small unit-cell volume, the strong itinerancy of f electrons leads to a mixed-valence state. The criterion for forming a heavy-fermion material is that the unit cell



**Figure 7.** The lattice parameters  $a$  and  $c$  of  $CeRu_{2-x}Ni_xSi_2$  versus  $x$ . The inset shows the valence  $v$  of Ce versus the unit-cell volume and the linear coefficient  $\gamma$  of the specific heat for the  $CeRu_{2-x}Ni_xSi_2$  system.

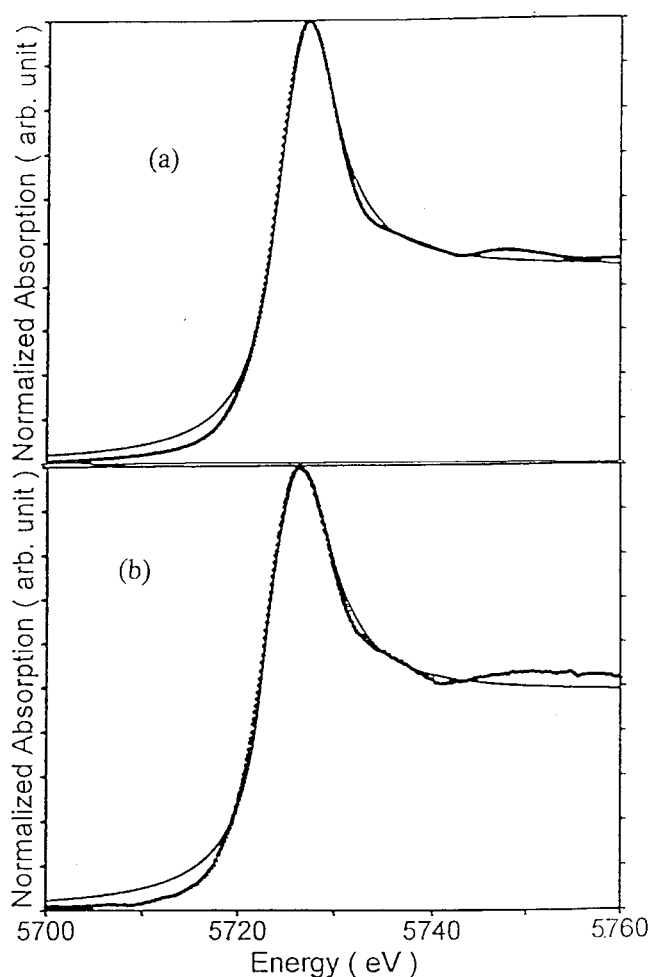
must have a size such that there is a delicate balance between the RKKY interaction and the Kondo effect. Only for a very narrow range of unit-cell volumes ( $165 \text{ \AA}^3 < V < 185 \text{ \AA}^3$ ) can heavy-fermion systems be found. For  $x < 0.4$ ,  $CeRu_{2-x}Ni_xSi_2$  exhibits HF characteristics. The unit-cell volume  $V$  of  $CeRu_{2-x}Ni_xSi_2$  with  $0 < x < 0.4$  has the range  $168 < V < 173 \text{ \AA}^3$ . The unit-cell volume  $V$  of  $CeCu_{2-x}Ni_xSi_2$  with  $0 < x < 0.5$  has the range  $164 < V < 170 \text{ \AA}^3$ . For both  $CeRu_{2-x}Ni_xSi_2$  and  $CeCu_{2-x}Ni_xSi_2$ , the unit-cell volumes in the heavy-fermion states are quite consistent with the limitation  $165 \text{ \AA}^3 < V < 185 \text{ \AA}^3$ . For  $x > 0.8$ , the unit-cell volume of  $CeRu_{2-x}Ni_xSi_2$  is too small for the formation of a heavy-fermion state.

Godart *et al* [8] reported the first-nearest-neighbour environment of Ce in  $CeRu_2Si_2$ . For each Ce in  $CeRu_2Si_2$ , there are eight transition metal Ru at a distance of  $[(a/2)^2 + (c/4)^2]^{1/2}$  and eight Si at a distance of  $[a^2/2 + (1/2 - z)^2c^2]^{1/2}$  with  $z = 0.370$  [25]. With the same  $z = 0.370$ , in  $CeRu_{2-x}Ni_xSi_2$ , the distance Ce-(Ru, Ni) =  $0.5[a^2 + 0.25c^2]^{1/2}$  and the distance Ce-Si =  $0.71[a^2 + 0.034c^2]^{1/2}$ . In  $CeRu_{2-x}Ni_xSi_2$  for  $x < 0.4$ , a notable increase of the lattice constant  $a$  will significantly enhance both the distance Ce-(Ru, Ni) and the distance Ce-Si, and will significantly reduce the hybridization of the f-electron wave function with the sp or s wave function of the neighbouring atom. The reduced localization of f electrons will change  $CeRu_{2-x}Ni_xSi_2$  from MV to HF.

In  $CeRu_2Si_2$ , eight Ru and eight Si atoms surround one Ce. Band-structure calculations [26] show that the electronic structure of  $CeRu_2Si_2$  is mainly determined by Ru. However, further experimental work is needed to support the above argument. For example, if the Ce

$L_{III}$ -edge spectra for  $CeRu_2Si_{2-x}Ge_x$  are not substantially changed by substituting Si for Ge, the hybridization of the f-electron wave function of Ce with the s wave function of Si might not be responsible for the HF and MV behaviours of  $CeRu_{2-x}Ni_xSi_2$ .

The Ce  $L_{III}$  absorption spectra of  $CeRu_2Ge_2$  and  $CeRu_2SiGe$  at 300 K are shown in figure 8. The solid lines in figure 8 are fitting curves. The details of the fitting procedure have been discussed in the reports of Liang [13] and Croft *et al* [16]. The valence of Ce in  $CeRu_2Ge_2$  is  $\sim 3.01$ , in  $CeRu_2SiGe$  it is  $\sim 3.03$ , and in  $CeRu_2Si_2$  it is  $\sim 3.03$ . Although the linear specific-heat coefficient ( $\gamma \sim 350 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ) of  $CeRu_2Si_2$  is much larger than that of  $CeRu_2Ge_2$  ( $\gamma \sim 20 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ) and that of  $CeRu_2SiGe$  ( $\gamma \sim 50 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ), the XAS spectra and the valences of Ce in  $CeRu_2Si_2$ ,  $CeRu_2SiGe$ , and  $CeRu_2Ge_2$  are almost the same. Therefore, the large linear specific-heat coefficient is not due to the hybridization of the f-electron wave function of Ce with the s wave function of Si. Therefore, in the system of  $CeRu_{2-x}Ni_xSi_2$ , the evolution from heavy-fermion to mixed-valence behaviour might be caused by the hybridization between the Ce 4f band and the Ru valence band.



**Figure 8.** The Ce  $L_{III}$  absorption spectra of (a)  $CeRu_2Si_2$  and (b)  $CeRu_2SiGe$  at 300 K. The solid lines are fitting curves (references [9] and [16]).

## 5. Conclusions

In contrast with the case for  $CeCu_{2-x}Ni_xSi_2$ , for  $CeRu_{2-x}Ni_xSi_2$  the lattice constant  $c$  is almost a linear function of  $x$ , whereas there is a deviation from linearity for the lattice constant  $a$  when  $x < 0.4$ . The  $\gamma$ -value of  $CeRu_{2-x}Ni_xSi_2$  is enhanced rapidly for  $v < 3.08$ . Therefore,  $CeRu_{2-x}Ni_xSi_2$  crosses from a heavy-fermion to a mixed-valence state at  $v \sim 3.08$ . There is no critical lattice constant  $c$  that separates the strongly mixed-valence regime from the heavy-fermion regime for  $CeRu_{2-x}Ni_xSi_2$ . The unit-cell volume  $V$  of  $CeRu_{2-x}Ni_xSi_2$  with  $0 < x < 0.4$  has the range  $168 < V < 173 \text{ \AA}^3$  which is quite consistent with the limitation  $165 \text{ \AA}^3 < V < 185 \text{ \AA}^3$ .

$L_{III}$  x-ray absorption spectroscopy investigations of  $CeRu_2Si_{2-x}Ge_x$  ( $x = 0, 0.5, 1$ ) indicate that the Ce-valence values do not significantly change when the Si of  $CeRu_2Si_2$  is substituted for with Ge. Hence, the Ce-valence values of  $CeRu_2Si_{2-x}Ge_x$  might not be due to the hybridization between the Ce 4f-electron wave function and the s wave function of Si. Therefore, in the  $CeRu_{2-x}Ni_xSi_2$  system, the hybridization between the Ce 4f-electron wave function and the Ru sp wave function might be responsible for the evolution from heavy-fermion to mixed-valence behaviour.

## Acknowledgments

This work was supported by the National Science Council of the Republic of China under Contract No NSC 89-2112-M-006-020.

## References

- [1] For a review, see Stewart G R 1984 *Rev. Mod. Phys.* **56** 755
- [2] For a review, see Lawrence J M, Riseborough P S and Parks R D 1981 *Rep. Prog. Phys.* **44** 1
- [3] Meisner G P, Giorgi A L, Lawson A C, Stewart G R, Willis J O, Wire M S and Smith J L 1985 *Phys. Rev. Lett.* **53** 1829
- [4] Koelling D D, Dunlap B D and Crabtree G W 1985 *Phys. Rev. B* **31** 4966
- [5] Sampathkumaran E V and Vijayaraghavan R 1986 *Phys. Rev. Lett.* **56** 2861
- [6] Gupta L C, MacLaughlin D E, Tien Cheng, Godart C, Edwards M A and Parks R D 1983 *Phys. Rev. B* **28** 3673
- [7] Haen P, Flouquet J, Lapierre F, Lejay P and Remenyi G 1987 *J. Low Temp. Phys.* **67** 391
- [8] Godart C, Umarji A M, Gupta L C and Vijayaraghavan R 1986 *Phys. Rev. B* **34** 7733
- [9] Ammarguella C, Escorne M, Mauger A, Beaurepaire E, Ravet M F, Krill G, Lapierre F, Haen P and Godart C 1987 *Phys. Status Solidi b* **143** 159
- [10] Gupta L C and Malik S K (ed) 1988 *Theoretical and Experimental Aspects of Valence Fluctuation and Heavy Fermions* (New York: Plenum)
- [11] Kuentzler R, Dossmann Y, Sampathkumaran E V, Dhar S K and Vijayaraghavan R 1987 *Phys. Rev. B* **36** 788
- [12] van der Meulen H P, de Visser A, Franse J J M, Berendschot T T J M, Perenboom J A A J, van Kempen H, Lacerda A, Lejay P and Flouquet J 1991 *Phys. Rev. B* **44** 814
- [13] Liang G 1990 *PhD Dissertation* Rutgers, The State University of New Jersey, New Brunswick, NJ
- [14] Falicov L M, Hanke W and Maple M B (ed) 1981 *Valence Fluctuation in Solid* (New York: North-Holland)
- [15] Wachter P and Boppert H (ed) 1982 *Valence Instabilities* (Amsterdam: North-Holland)
- [16] Neifeld R A, Croft M, Mihalisin T, Segre C U, Magigan M, Torikachvili M S, Maple M B and Delong L E 1985 *Phys. Rev. B* **32** 6928
- [17] Croft M, Neifeld R A, Segre C U, Raan S and Parks R D 1984 *Phys. Rev. B* **30** 4164
- [18] Edwards M A, Horn S and Parks R D 1987 *Solid State Commun.* **61** 65
- [19] Tsunekawa M, Suga S, Kimura A, Matsushita T, Ueda S, Daimon H, Imada S, Nakatani T, Saitoh Y, Iwasaki T, Sekiyama A, Fujimori A, Ishii H, Miyahara T, Hanyu T, Namatame H, Taniguchi M, Shigemasa E, Sakai O, Takayama R, Settai R, Azuma H and Onuki Y 1997 *Solid State Commun.* **103** 659
- [20] Liang G, Perez I, DiMarzio D, Croft M, Johnston D C, Anbalagan N and Mihalisin T 1988 *Phys. Rev. B* **37** 5970
- [21] Mihalisin T, Scoboria P and Ward J A 1981 *Phys. Rev. Lett.* **46** 862

- [21] Amato A, Baines C, Feyertherm R, Flouquet J, Gygax F N, Lejay P, Schenck A and Zimmermann U 1993 *Physica B* **188** 276
- [22] Hill H H 1970 *Plutonium 197 and Other Actinides* ed W N Miner (New York: AIME)
- [23] Sampathkumaran E V, Kalkowski G, Laubschat C, Kaindl G, Domke M, Schmiester G and Wortmann G 1985 *J. Magn. Magn. Mater.* **47+48** 212
- [24] Loidl A, Knopp G, Spille H, Steglich F and Murani A P 1989 *Physica B* **156+157** 794
- [25] Loidl A, Knorr K, Knopp G, Krimmel A, Caspary R, Böhm A, Sparn G, Geibel C and Steglich F 1992 *Phys. Rev. B* **46** 9341
- [26] Runge E K R, Albers R C, Christensen N E and Zwicky G E 1995 *Phys. Rev. B* **51** 10375